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The *K* X-ray absorption edge of aluminum in metal and oxide

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With 5 figures in the text

ABSTRACT

The Al *K* absorption edges of technical and pure aluminum metal and aluminum oxide (Al_2O_3) have been recorded and measured. The fine structure very close to the *K* absorption edge of metallic aluminum earlier reported by Cauchois (1952) has not been found. The width of the *K* level of aluminum and the energy gap of aluminum oxide are determined. There is a great similarity between the *K* absorption edge and the high frequency edge of the emission line ($K\beta$) of the aluminum metal as well as between the edges of the aluminum oxide. The wavelength values of the former edges agree within the limits of error.

Introduction

The Al *K* X-ray absorption edge in metal has been measured earlier by Sandström in 1935 [1], by Munier, Bearden & Shaw in 1940 [2] and by Cauchois in 1952 [3]. The Al *K* absorption edge in both metal and oxide has also been measured by Das Gupta [4].

Sandström used a bent crystal spectrograph with a quartz crystal and photographic registration of the intensity, Munier, Bearden & Shaw a double crystal spectrometer with an aqua-marine crystal and registration with a Geiger–Müller counter. Cauchois, finally, used a bent crystal spectrograph with gypsum and mica crystals and photographic registration. The present investigation only extends over the primary absorption edges; the Kronig structure has been entirely neglected. Absorption and emission measurements together give information about the density of electron states in the conduction band of Al and valence band of Al_2O_3. Emission measurements of the *K* spectrum of Al and Al_2O_3 were recently undertaken by Nordfors [5].

To get good X-ray intensity a method described by Nordfors, Rudström and Sandström [6] was used. At wavelengths of about 8 Å, which are used here the second order wavelength, third order wavelength and fourth order wavelength are excited at 3.2 kV, 4.8 kV and 6.4 kV respectively. A voltage of 6.00 kV was applied to the X-ray tube and this doubles the first order intensity as compared to 3.2 kV. The contents of higher order radiation are determined with Al filters and corrections worked out.

Apparatus

The present investigation was undertaken with a large bent crystal spectrograph designed by Sandström [7]. A quartz crystal ($10\bar{1}0$) was employed. Good stabilization of the voltage (6 kV) of the X-ray tube and of the emission current (40 mA) was

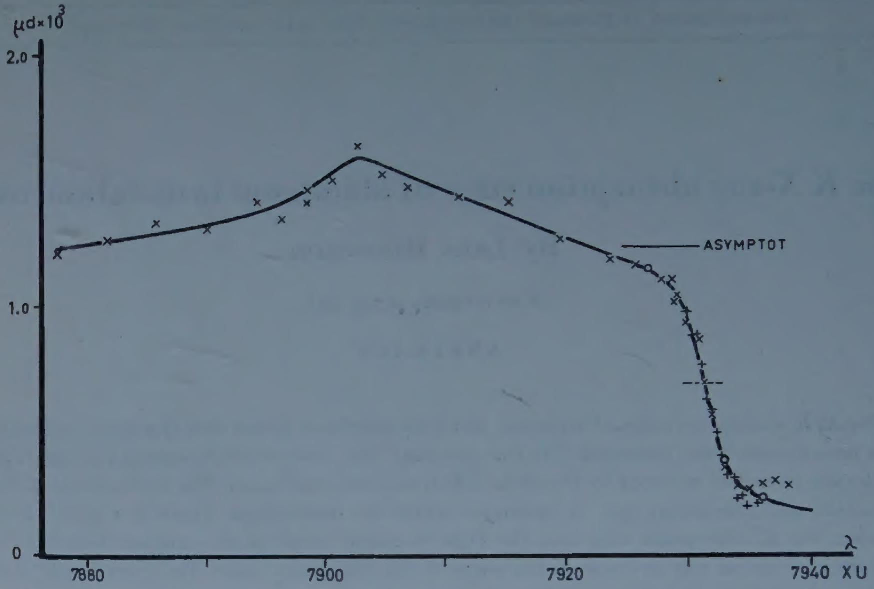

Fig. 1. The *K* X-ray absorption edge of technical aluminum. The point of inflection is shown by a horizontal line.

achieved by stabilizing circuits earlier used with the spectrograph. A vacuum below 2×10^{-5} mm Hg was kept during the measurements. A Geiger–Müller tube was used for the registration of the X-rays and it had a mylar window of the thickness of 5 μ (Sandström, Nordfors [8]). The alcohol–argon filling earlier used was substituted by an argon–butane filling. This was easier to handle and as the tube had to be refilled every day, this mixture was convenient and involved no risk of inhomogeneity. Alcohol also has the drawback of diffusing through thin films with a subsequent destruction of the counter plateau. It was found that at a total pressure of 200 mm Hg the proportion of 95% argon and 5% butane gave the best plateau (length 300 volts, slope 0.02%/volt).

The X-ray tube designed by Nordfors [5] has two cathodes, consisting of oxide coated platinum spirals, which could be switched on one at a time, and two corresponding targets of tungsten and silver. The former gave the continuous X-ray radiation for the absorption measurements and the latter the emission lines for wavelength reference. The intensity of the continuous radiation was about 800 impulses/min (1st order).

Technical aluminum

First an investigation of technical Al was carried out. The earlier absorption measurements of Al has been made with metal of this kind. The absorbing screen consisted of two 0.5 μ foils pressed together and fastened to a rectangular frame that could be brought into the passway of the X-rays. The homogeneity of the composed foil was tested for different settings of the frame by the Ag $L\beta_1$ line. The thickness was also checked this way. The impurities of technical Al consist of iron, copper and silicon up to 1%.

The result of the K X-ray absorption edge measurements of technical Al is illustrated in Fig. 1. The different kinds of dots belong to separate runs. The mutual consistency between the positions of the measured points gives information about the reproducibility. The circular points are measured for an especially long time and an arctangent curve fitted to them.

The width of the edge has been determined according to the suggestion by Richtmeyer, Barnes & Ramberg [9]. The width is thus determined so as to correspond to points of $\frac{3}{4}$ and $\frac{1}{4}$ of maximum absorption (the upper asymptote of the arctangent curve). The wavelength of the absorption edge is determined corresponding to the inflection point of the arctangent curve.

In all wavelength determinations the reference line has been Ag $L\beta_1$ in the second order. Corrections for refraction and anomalous dispersion have been made. Ag $L\alpha_1$ in the second order has been used together with Ag $L\beta_1$ to determine the dispersion. Data of the absorption edge are given in Table 1.

Pure aluminum

The foils in this case were rolled from spectroscopically standardized aluminum metal from Johnson, Matthey & Co. As impurities from the roller had to be avoided and as at a certain stage the foils got stuck and damaged they were put between filter-papers, which had earlier been rolled to smooth their rough texture. Two foils of thickness 1.1 μ and 0.8 μ were used in the measurements. The thickness was calculated by weighing assuming that the density of the foils is the same as that of the bulk material.

Depending on the relatively great thickness of the 1.1 μ foil, points on the high absorption side of the edge were recorded during a much longer time than the rest in order to give about the same statistical error in the absorption coefficient (Soules & Shaw [10]). The absorption curve shown in Fig. 2 gives the mean value of two separate runs which on the high absorption side of the edge corresponds to a total of 35000 incident impulses per point (1st order radiation). The incident intensity was checked for every point to detect variations due to a change of the focal spot of the electrons or a change of the plateau of the G-M tube. The stability was very good, however, and the fluctuations that appeared were entirely statistical. Fig. 2 shows the absorption edge, when the 1.1 μ foil was inserted. An absorption minimum in the Kronig structure (designated S_2) was recorded using the 0.8 μ foil. Measurements with the latter foil were also performed in the neighbourhood of the principal edge with good agreement to the absorption curve of the 1.1 μ foil.

Table 1. Al K X-ray absorption edge data from different absorbers.

The constants used are: 1 X.U. $= 1.00202 \times 10^{-11}$ cm, 1 $\text{Ry}_\infty = 109737.3$ cm^{-1}. The energy conversion factor is 12372.2×10^3 (X.U.)·(eV).

Absorber	Position of the edge		γ/R	Width, uncorrected for finite resolving power eV
	X.U.	eV		
Technical aluminium	7931.20 ± 0.40	1559.9	114.665	0.66 ± 0.05
Pure aluminum	7931.66 ± 0.40	1559.9	114.658	0.66 ± 0.05
Aluminum oxide	7904.70 ± 0.40	1565.2	115.049	

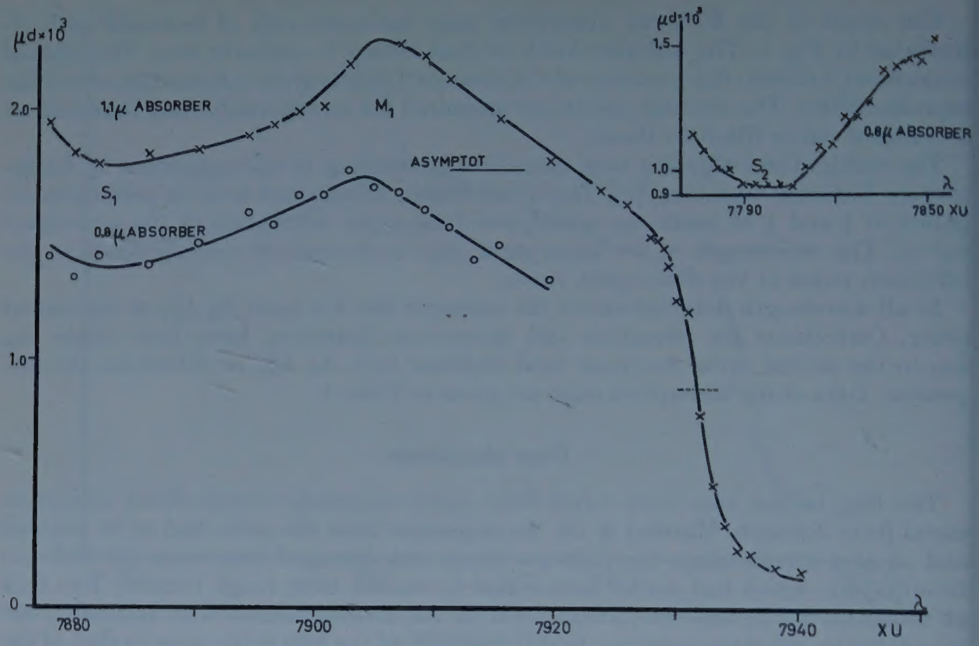

Fig. 2. The *K* X-ray absorption edge of pure aluminum. Two foils of the thickness of 1.1 μ and 0.8 μ are used. The dotted line indicates the inflection point of the arctangent curve.

Table 2. Fine structure close to the edge.

Distance from the principal edge (in eV).

Denomination	Sandström	Munier, Bearden & Shaw	Cauchois	Present
S_1 S_2	9.9 27.2	11.5 28.0	9.0 28.8	9.4 26.9

Aluminum oxide (Al_2O_3)

The foils in this case were made by electrolytic oxidation of rolled pure Al foils. The foil was fastened in good contact with a rectangular frame (about 3 cm² opening) and used as an anode. A lead plate served as a cathode. Oxalic acid (5%) served as electrolyte. The temperature was kept constant at 20°C. The tension applied did not exceed 50 volts and the current was held below 400 mA. If from the beginning the frame with the foil was completely lowered in the electrolyte and the current switched on, the parts of the foil near the frame first changed into oxide (because of the higher potential there), thereby stopping the current flow to the middle part and thus stopping further oxidation there, leaving metallic aluminum grains. This effect was overcome by slowly (0.2 mm/min) lowering the frame with a screw gadget into the electrolyte. In this way almost no metallic aluminum was isolated. By this method

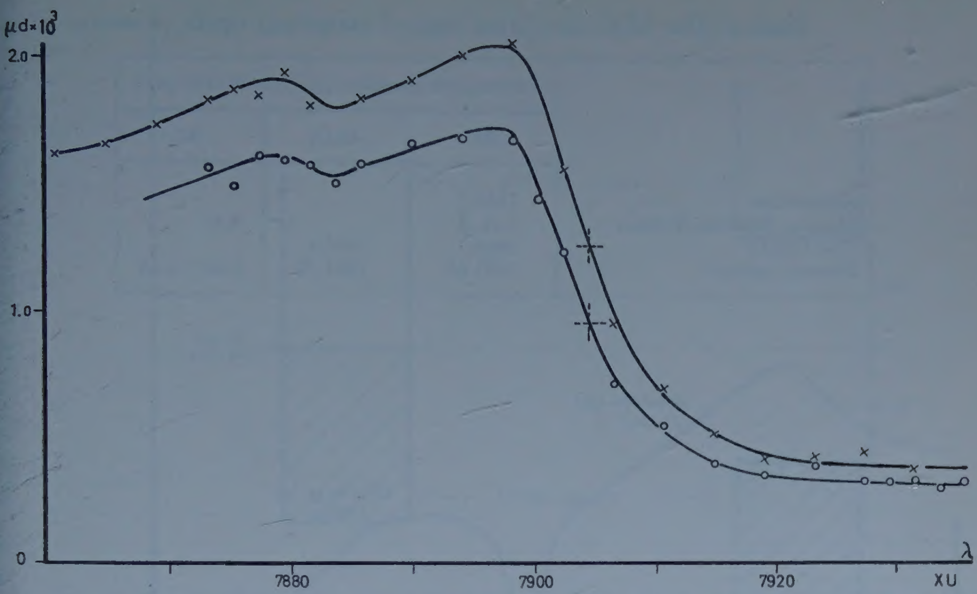

Fig. 3. The *K* X-ray absorption edge of aluminum oxide (Al_2O_3). ×, absorption curve of the oxidized 1.1 μ foil; ○, absorption curve of the oxidized 0.8 μ foil. The dotted lines indicate the wavelength positions of the edges.

pure rolled metallic aluminum foils of the thickness of 0.8 μ and 1.1 μ were turned into oxide. They were afterwards cleaned by washing in cold distilled water. An investigation of the X-ray diffraction of the foils showed that the oxide is essentially amorphous.

The *K* X-ray absorption edge of Al_2O_3 is seen in Fig. 3. The principal edge is not so steep as that of metallic Al. The curve has two maxima just on the high frequency side of the edge. As no arctangent curve can be fitted to the principal edge of the oxide, the wavelength of the edge is here determined at the point of half maximum absorption. Table 1 gives the mean value of the edges of the two curves in Fig. 3.

Results and discussion

The *K* X-ray absorption curve of technical aluminum has its edge shifted 0.46 X.U. towards shorter wavelengths as compared to that of pure aluminum. The agreement is evidently very good and it is questionable if the difference is significant. The effect of greater oxide contamination in the technical foil would change the position of the edge towards smaller wavelengths. The technical foil was put together from two foils and thus had four oxidized surfaces, which had been exposed to air for years. The pure aluminum foil was kept only for a few hours in the air. With this method of making foils it is evidently impossible to avoid the momentanous oxide film, which has a thickness of 0.01 μ.

Cauchois has reported [3] two minima of absorption (designated 0 and 00) between the principal edge and the maximum M_1 of the absorption curve in Fig. 2. Cauchois used a mica crystal to get high dispersion. This crystal contains aluminum and it

Table 3. The Al *K* absorption edge of metal and oxide.

	Wavelength position (X.U.)		Width (eV)
	Al	Al_2O_3	Al
Sandström	7935.1		
Munier, Bearden & Shaw	7.95 Å		0.35
Das Gupta	7935.7	7905.4	
Present results	7931.66	7904.70	0.66 ± 0.05

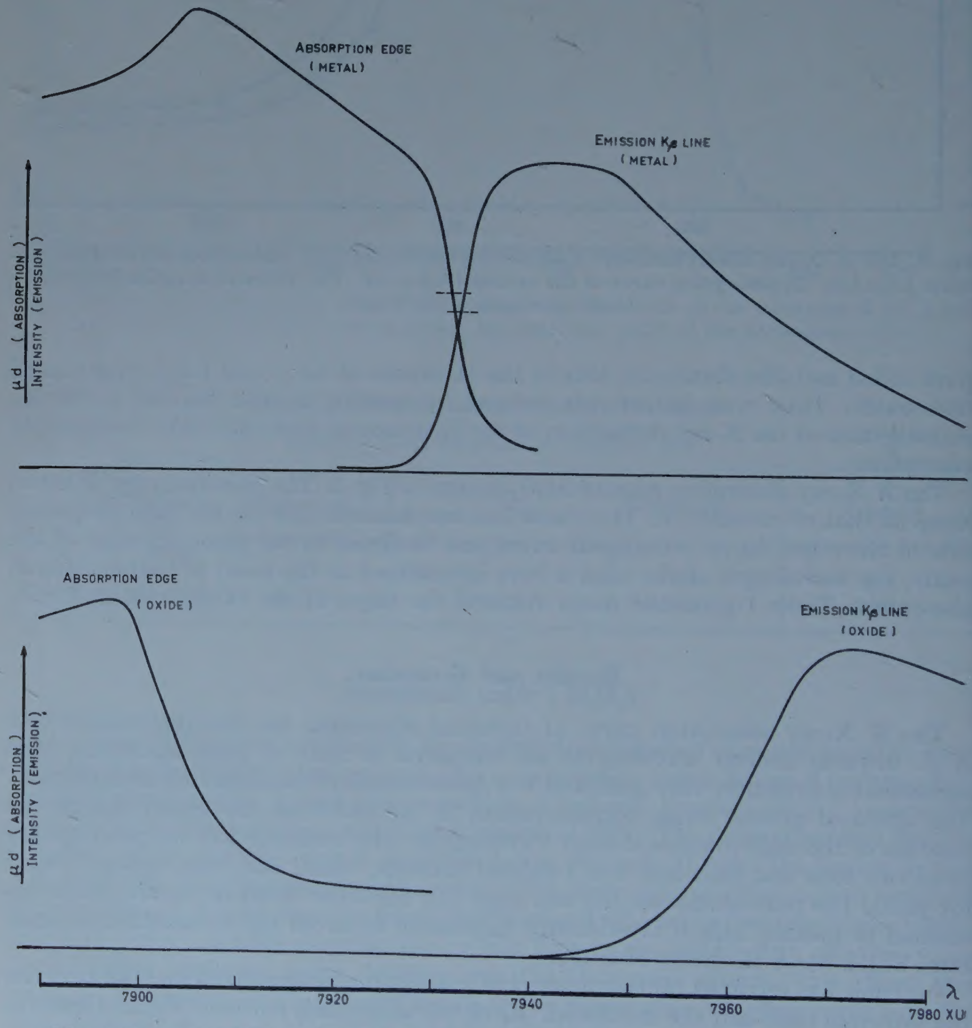

Fig. 4. Composite plot of absorption and emission edges of aluminum metal and oxide.

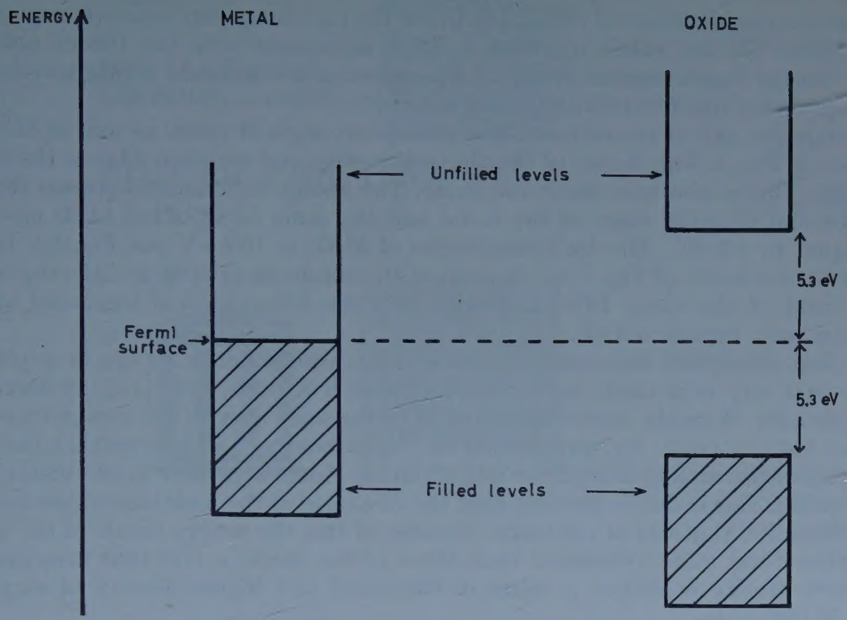

Fig. 5. Energy level scheme of aluminum metal and oxide.

may be expected to give an absorption spectrum of its own in the region of the Al *K* edge and may thus distort the shape of the true absorption curve of the foil. To evaluate this effect, Cauchois made special studies of the absorption spectra of aluminum in a mica sheet (as an absorber) and the spectrum of continuous radiation reflected by the mica crystal analyser. The experiments showed that the mica crystal analyser did not have any influence in a region of 7 eV from the principal edge. The present records show no such structure, however. The resolving power of the spectrograph, $\lambda/\Delta\lambda = 5200$, $\Delta\lambda = 1.5$ X.U. (Sandström [11]), is good enough to reveal this structure well and there cannot be any thickness effect that obliterates the structure.

The width of the absorption edge as here determined should give the width of the *K* level of aluminum, if the small influence of finite resolving power is neglected. If the steepness of the emission line towards shorter wavelengths is considered as a measure of the width of the *K* level, the level is found to be of about the same width as in the first case.

By the band theory of metals the *K* absorption edge corresponds to electron transitions from the *K* level to the unfilled part of the conduction band and the emission curve corresponds to transitions from the filled portion of the conduction band to a hole in the *K* level. The boundary between the filled and unfilled region is the Fermi surface. The absorption starts when the energy of the incident photons is exactly great enough to bring an electron from the *K* level just up to the Fermi surface. On the other hand the electrons just below the Fermi surface give the high frequency edge of the emission curve. As in a metal there is no gap between the unfilled and filled bands of levels the absorption and high frequency emission edges should have the same wavelength position.

The present result of 7931.66 X.U. for the absorption edge of pure aluminum metal and the wavelength value of 7932.20 X.U. for the high frequency emission edge given by Nordfors [5] are, taken together, in good agreement with the theory outlined above. Earlier measurements of the Al $K\beta_x$ emission line indicate higher wavelength values probably due to oxidation of the target [5].

A composite plot of the emission and absorption edges of metal as well as of oxide is shown in Fig. 4. The shapes of the absorption edge and emission edge of the metal are alike. This is also true about the oxide. The energy differences between the absorption and emission edges of the metal and the same edges of the oxide are alike and equal to 5.3 eV. The forbidden region of Al_2O_3 is 10.6 eV (see Fig. 5.). In the energy level scheme of Fig. 5 the bottom of the conduction band and the top of the filled band of the oxide differ in energy from the Fermi level of the metal by the same amount, namely 5.3 eV.

The first absorption maximum M_1 in the Al_2O_3 absorption curve can be explained in the same way as in many metal oxides (Coster & Kiestra, 1948 [12]) by assuming a high density of empty electronic states of p symmetry just at the beginning of the unfilled valence band. By the method of "tight binding" it follows that the perturbation of the atomic fields from neighbouring atoms is greater in the metal than in the oxide. This is due to the fact that the Al atoms of the metal are closer to each other than the Al atoms of the oxide. Because of this the energy bands of the metal are broader and more hybridized than those of the oxide; a fact that accounts for the lower density of empty p states in the metal and higher density of empty p states in the oxide.

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